INTEGRATION OF THE EQUATION OF PEAK MOTION IN PROGRAMMED-PRESSURE AND –TEMPERATURE GAS CHROMATOGRAPHY

INTEGRACION DE LA ECUACION DE MOVIMIENTO DE PICO EN CROMATOGRAFIA GASEOSA CON PRESION Y TEMPERATURA PROGRAMADAS

F.R. González[1], A.M. Nardillo[2]

SUMMARY

Numerical procedures for the estimation of the retention are compared considering the simultaneous programming of temperature and column head pressure , embracing issues from the mathematical basis to the practical aspects in the simulation of the chromatographic process by computer.

Keywords: *programmed-pressure and –temperature gas chromatography; retention models; computer simulation; alkanes; hydrocarbons.*

INTRODUCTION

The equation of peak motion in programmed pressure and temperature gas chromatography (PPTGC) may be written in terms of four well defined and accessible functions **[1]**:

$$\frac{dz}{dT} = \frac{L}{f'(T)\, Q(z,T)\, t_M(T)\, [1+k(T)]} \qquad (1)$$

where the variables of the equation (z,T) are the axial position of the peak in the column and the absolute temperature. The parameter L is the length of the column . The function $f'(T)$ is the first derivative of the relationship between time and temperature, $T=f(t)$, that describes the temperature program selected by the chromatographer. This relationship is an external restraint imposed to the system , fixing how the temperature will evolve in time. In the most general situation f' may be a function of T. In the particular case of linear temperature programs is a parameter : the heating rate r_T. Another restraint is the head pressure program $p_i(t)$ or $P(t)$ (where $P = p_i / p_o$). It can also be expressed as a function of T **[1]**, $P=P(T)$. The outlet pressure of the column p_o is usually a constant. The pressure program $P(T)$ cannot always be selected voluntarily. In chromatographs without pressure programming capabilities, $p_i(T)$ is a

[1] División Química Analítica, Facultad de Ciencias Exactas, Universidad Nacional de La Plata
[2] Miembro de la Carrera del Investigador del CONICET; Profesor Asociado, UNLP

characteristic function of the flow control system **[1]**. Therefore, as a matter of fact, all chromatographs have some intrinsic sort of pressure programming.

In the denominator of Eq.(1), $Q(z,T)$ function is the local velocity factor. This is the ratio between the average carrier gas velocity along the column at temperature T, $\bar{u}(T)$, and the local velocity of the carrier gas at position z , $u(z,T)$[3]: $Q(z,T) = \dfrac{\bar{u}(T)}{u(z,T)}$. If the isothermal motion of the carrier gas is described by the differential form of Hagen- Poiseulle Equation, in the case of capillary columns ; or by D'Arcy's Equation in packed columns, then :

$$u(z) = -\frac{B}{\eta}\frac{dp}{dz} \tag{2}$$

where η is the viscosity of the gas and p the absolute local pressure at z position. B can be assumed to be a constant of the system **[1]**. From Eq. (2) we derive the following expression for Q (see for example reference **[2]**):

$$Q = \frac{3}{2}\frac{(P^2-1)}{(P^3-1)}\left[P^2 - \frac{z}{L}(P^2-1)\right]^{1/2} \tag{3}$$

The current theory of programmed temperature assimilates the chromatographic process to a sequence of consecutive isothermal states, so P will be the pressure program $P(T)$ and Q will depend definitely as $Q(z,T)$. This basic hypothesis of the theory also implies that the process is assumed to be a summation of sequential steady state flows at successive temperatures , with an existing thermal equilibrium at each point .

The third function present in the denominator of Eq.(1) is the isothermal gas hold-up time $t_M(T)$. Resembling Q , $t_M(T)$ is also a function of the pressure program $P(T)$; and in the same way, from Eq. (2) we can derive the expression for this function **[1]**:

$$t_M(T) = \frac{T^N}{C_t P_o}\,\frac{[P^3(T)-1]}{[P^2(T)-1]^2} \tag{4}$$

where C_t is another constant of the system .

Finally, the fourth function present in the denominator of Eq.(1) is the capacity factor $k(T)$ describing the thermodynamics of the process:

$$k = \frac{1}{\beta}\,exp\left[-\frac{\Delta G^{\circ}(T)}{RT}\right] \tag{5}$$

---

[3] The local velocity of the carrier gas u ,as usually is indicated in GC , is the crossectional average of the radial profile of the axial velocity v_z in the column: $u = \langle v_z \rangle$ (see for example ref.[3]).

The standard partial molar free energy of solution ΔG° is a function of T and p. The dependence on pressure can be neglected in chromatographic conditions. The phase ratio of the column β may be considered a constant if the thermal expansion of column materials is neglected too , hypothesis that was necessary for accepting B and C_t as constants.

Equation (1) is the differential equation governing the motion of the band. This motion is the resultant from the combination of a fluid dynamic effect, the transportation of the band by means of the gas stream, and the thermodynamics of interaction between the solute and the stationary phase. As shown, the fluid dynamics of the chromatographic process is defined by functions $Q(z,T)$ and $t_M(T)$; depending naturally on both: the pressure program and the temperature program. The differential equation can be solved by direct variable separation only when P is constant, as consequence of the function Q depending simultaneously on z and T if P changes with temperature. When using the constant inlet pressure mode of flow control, the integration of the equation after direct variable separation leads to the well known relationship for linear temperature programs **[4]**:

$$r_T = \int_{T_0}^{T_R} \frac{dT}{t_M(T)\ [1+k(T)]} \tag{6}$$

where T_0 and T_R are the initial and the retention temperature, respectively. Otherwise , by changing to the variable t, the equivalent expression is **[5]**:

$$1 = \int_{0}^{t_R} \frac{dt}{t_M\ (1+k)} \tag{7}$$

where t_R is the retention time of the solute.

Historically, in conditions of variable pressure drops with temperature, rigorous retention estimation initiated from general Eq. (1) has been carried out avoiding the mathematical difficulty of the simultaneous dependence of Q on z and T by means of a defined numerical procedure of calculation. The classical example is the strict treatment developed by Dal Nogare and Langlois **[6]**, specifically for the constant mass flow mode of carrier gas control[4], although it has general applicability. We shall identify the algorithm with the general expression **[6]**:

$$t_R = \int_{0}^{L} \frac{[1+k(T)]\,dz}{u(z,T)} \tag{8}$$

In this algorithm the local velocity $u(z,T)$ has to be calculated at each incremented value of z. A stepwise numerical integration of eq.(8) begins when $z=0$ and $T = T_0$, then the local velocity can be calculated at the initial position by means of the general equation:

[4] In current chromatographic conditions , this mode of flow control behaves like a special case of linear head pressure programming [7] .

$$u(z,T) = \frac{L}{Q(z,T)\, t_M(T)} \tag{9}$$

Incrementing z in dz leads to an incremented elapsed time (from injection) given by the stepwise integration of Eq.(8), (determining k by using the initial temperature in Eq.(5) for the first cycle of calculation):

$$t = \int_0^z \frac{[1+k(T)]\, dz}{u(z,T)} \tag{10}$$

The sum is performed up to the actual position z. Now the effective temperature at the incremented z can be obtained from the temperature program $T=f(t)$. With this temperature another cycle of calculation is possible: incrementing z, determining u and k from Eqs. (9,5), actual t from Eq.(10) and actual T from $f(t)$. The cycle is repeated until the incremented z reaches the value of L, as it is indicated in Eq. (8). Then the time elapsed at this point is the retention time t_R, and $T=f(t_R)$ is the retention temperature T_R. These are the unknown parameters, object of the calculation. If desired, the procedure allows listing T as a function of z, or vice versa. Therefore, it makes the solution of Eq. (1) attainable, which is a curve in the plane z-T or z-t (the integral curve). Notwithstanding, the chromatographic interest is only centred on obtaining t_R . In Fig. 1 are shown integral curves belonging to the solute *n*-dodecane, calculated through the described procedure with conditions indicated in Table 1. The influence of the temperature program parameter on the solution of Eq. (1) is illustrated (in other words, the influence of the $T=f(t)$ function on the movement of the band).

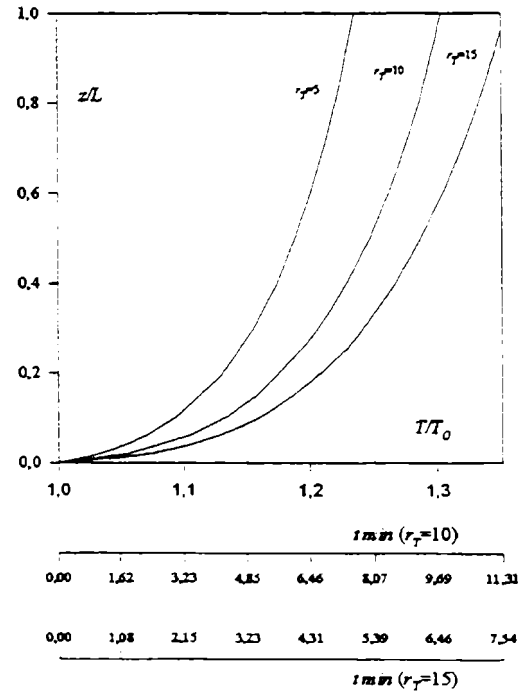

Fig. 1.- Peak position as a function of column temperature (reduced variables) or time (min). The integral curves belong to *n*-dodecane in the chromatographic conditions indicated in Table 1 and [7]. These were calculated through the classical algorithm of [6].

Table 1

Comparison of calculated retention times using constant mass flow mode of carrier gas control

Solute	1. t_R (min) Eq.(11)	2. t_R (min) algthm. Ref.[6]	3. $\int_0^L Q/L\,dz$ algthm. Ref.[6]
n-Octane	4.310	4.303	0.9974
p-Xilene	5.090	5.084	0.9968
1,3,5 Trimethylbenzene	6.430	6.424	0.9960
1-Undecene	8.320	8.313	0.9955
Naphthalene	9.400	9.391	0.9950
n-Dodecane	9.820	9.819	0.9952
n-Tetradecane	12.350	12.356	0.9951
n-Hexadecane	14.830	14.860	0.9957

Column 1: retention times estimated through Eq. (11).
Column 2: results calculated according to the classical algorithm [6].
Column 3: numerical integration of Q/L along z applying the same procedure of column 2.
Temperature program is a single ramp with r_T = 10 °C/min. , $T_0 = 50\ °C$, L=30 m (reported by the supplier), $p_o = 765$ Torr , initial p_i=1277 Torr . Applied $P(T)$, $t_M(T)$ and $k(T)$ functions , from Reference [7].

A recent example of programmed temperature retention simulation , involving the described stepwise calculation of the local velocity , is the work by Snijders, Janssen and Cramers **[8]**, which uses a procedure essentially equivalent to that followed in reference **[6]**, but applied to constant inlet pressure.

The objective of the present work is to demonstrate the validity of equations (6) and (7) under variable P(T) flow conditions, or more generally, the validity of the following retention expression for programmed pressure and temperature gas chromatography:

$$1 = \int_{T_0}^{T_R} \frac{dT}{f'(T)\, t_M(T)\, [1 + k(T)]} \tag{11}$$

The consequences of chromatographic interest, the advantages and limitations of this relationship, with respect to the procedure identified by Eq. (8), will be discussed .

DEMONSTRATION

General Eq.(1) can be rearranged to:

$$\frac{Q(z,T)}{L}\,dz \;-\; \frac{1}{f'(T)\,t_M(T)\,[1+k(T)]}\,dT = 0 \tag{12}$$

which fits the generic form of :

$$M(x,y)\,dx \;+\; N(x,y)\,dy = 0 \tag{13}$$

The necessary and sufficient condition allowing Eq.(13) to be a exact differential is:

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} \tag{14}$$

The general solution of the exact equation is (see for example **[9,10]**):

$$\int M\,\partial x \;+\; \int\left(N - \frac{\partial\left(\int M\,\partial x\right)}{\partial y}\right)dy = C \tag{15}$$

where C is an integration constant.

In our specific case: $dx \equiv dz$, $dy \equiv dT$, $M(z,T) \equiv Q(z,T)/L$, and

$$N(T) \equiv -\frac{1}{f'(T)\,t_M(T)\,[1+k(T)]}$$

Equation (12) is not in general an exact differential, since:

$$\frac{\partial N(T)}{\partial z} = 0 \neq \frac{\partial M(z,T)}{\partial T}$$

We want to determine if Eq.(12) becomes a exact equation when $z \to L$, considering that we are only interested in the particular solution with boundary condition: $(z=L\ ,\ T=T_R)$. Out of the limits $0 \le z \le L$ the equation has no physical meaning. Invariably, the integration begins at $z=0$, this being a condition *sinequa non*. It should be noted that the initiation of the integration at a point different to $z=0$ has not any physical meaning either .

As derivation and integration are inverse operations, we know that:

$$\frac{\partial M}{\partial T} = \frac{\partial\left[\dfrac{\partial\left(\int M\,\partial z\right)}{\partial z}\right]}{\partial T} \tag{16}$$

In the limit when $z \rightarrow L$, the primitive of M in the numerator of the right member of Eq. (16) is equal to:

$$j(T) = \frac{3\,[P^2(T)-1]}{2\,[P^3(T)-1]}$$

Then, its partial derivative respect to z is zero, and from Eq. (16) we see that in the proximity of $z=L$ is verified that $(\partial M / \partial T) = 0$. So, the condition of Eq. (14) is satisfied when $z \rightarrow L$, the equation of peak motion becoming a exact equation. Therefore, for the particular solution of chromatographic interest, Eq.(15) yields:

$$\int_0^L M\,\partial z + \int_{T_o}^{T_R}\left[N - \frac{\partial\left(\int_0^L M\,\partial z\right)}{\partial T}\right] dT = 0 \tag{17}$$

The integral $\int_0^L M\,\partial z$ can be solved analytically by substitution, with a result equal to unity.

Thus, Eq. (17) is reduced to Eq.(11), being our demonstration concluded .

The statement on the validity of Eq. (11) for variable $P(T)$ can also be demonstrated with a rather more limited formalism. The sufficient condition for Eq. (13) to be a exact differential is the existence of a function V such that: $\frac{\partial V}{\partial x} = M$ and $\frac{\partial V}{\partial y} = N$ (see for example **[10]**). The existence of V for the equation of peak motion (12) can be proven when $z \rightarrow L$.

CONSEQUENCES AND CORROBORATION

Numerical corroboration on the validity of Eq. (11) with variable $P(T)$ chromatographic conditions can be carried out from its consequences. Some of these are of fundamental importance with respect to the retention numerical simulation in programmed pressure and temperature gas chromatography.

Retention simulations through the algorithm resumed in Eq.* (8) *and by the numerical integration of Eq.* (11) *are equivalent

The statement is supported by the fact that both procedures concern the same basic chromatographic hypothesis relative to Eq. (1), not involving additional mathematical assumptions, approximations or simplifications, one with respect to the other, as demonstrated in the preceding section. Corroboration of this statement can be easily achieved by comparing numerical results obtained through both procedures. These should arrive to the same values under variable *P(T)* conditions. In Table 1 are shown calculated retention data for the constant mass flow control mode, following the respective procedures. The expressions of the applied functions and the conditions in the calculations for each solute can be found in Reference **[7]**. One of the reasons why they do not yield *exactly* the same values is the discrepancy in the number of operations performed by the computer. In the case of Eq. (11) less operations must be performed. However, this would be a minor contribution to the observed differences, taking into account that machine round-up has a minimal incidence in the numerical results. Furthermore , the forms of the integrands in equations (8) and (11) are quite dissimilar, generating different errors along the numerical integration, even if the same integration method is applied to both. Probably, the most important contribution to the observed differences is the existence of the additional parameter L in the algorithm of Eq. (8), not present in Eq. (11). The contribution of the error of L may be significant if nominal values are entered into the calculation. Besides, there might be inconsistency between measured values of L and gas hold-up time. It should be noted that there is a functional interrelation between them that should be fulfilled .

Parameter L is irrelevant for retention estimation from $t_M(T)$ and k(T)

L becomes irrelevant for the retention calculation through Eq. (11), instead, for simulation by the algorithm of Eq. (8) is a necessary input. Note that the effect of column's length is already accounted for by the function t_M(T). If Eq. (11) is strictly applicable to variable *P(T)* , then in these conditions L should be irrelevant too. This fact was corroborated by present authors running programs according to Eq. (11) for different *P(T)* functions and comparing calculated retentions with the experimental values **[7]**, concluding that the errors are in the same order respect to algorithms that include L as a significant parameter .

The following equality is verified:

$$\int_0^L \frac{Q(z,T)\,dz}{L} = \int_0^L \frac{Q(z,T)}{L}\,\partial z = 1 \qquad (18)$$

The integral in the left member represents the sum performed with algorithm of Eq. (8), a stepwise numerical integration with simultaneous variation of z and T. The integral on the right is the analytical one keeping T constant, which is equal to unity. This statement derives directly from the demonstration of section 2 and the statement 1 from this section. Equation (18) represents a special property of the fluid dynamics of the GC system. It was first observed by Said and Stenberg as it is mentioned in **[11]** (p. 105). This relationship displays the reason why

L becomes irrelevant. In Table 1 are shown calculated values of the integral on the left, introducing the respective sentences in the computer program used for calculating the retention times and the integral curves. The discrepancies respect to unity show clearly the errors associated to the numerical integration and to the introduction of L, as was mentioned previously .

There are some precedents in the literature concerning the application of Eqs. (6) or (7) to chromatographic conditions pertaining to variable $P(T)$. For example, in the paper by Dose **[12]** the reported $t_M(T)$ function cannot be associated to a constant head pressure condition **[1]**.

CONCLUSIONS

The equation of peak motion only becomes a exact equation when $z \rightarrow L$, i.e. in the proximity of the particular solution of chromatographic interest ($z=L$) being applicable Eq. (15) only if the integration is performed along the whole domain of z. So, Eq. (11) would not yield correct results if it is applied to an integration to intermediate values of z. In other words, the strict mathematical solution of Eq. (1) (i.e. relating z as a function of T or t) is not possible with this procedure. Nevertheless, the chromatographic interest is centred exclusively on the value of t_R or T_R, and not in obtaining the integral curve T vs. z. Therefore, this could be appreciated as a minor limitation of the procedure. On the other hand, there is a neat advantage in not needing to enter the value of the parameter L with its intrinsic error. Furthermore, having few operations to be done results in simpler and faster computer programs , with a reduced amount of sentences. The most outstanding characteristic of Eq. (11) is that it can be written explicitly in terms of the pressure program $P(T)$, this being crucial for a simplified treatment in PPTGC **[7]**.

REFERENCES

[1] González, F.R.; Nardillo, A.M.- **J. Chromatogr. A, 757**, 97 (1997).
[2] Zhang, J.Y.; Wang, G.M.; Quian, R.- **J. Chromatogr., 521**, 71 (1990).
[3] Bird, R.B.; Stewart, W.E.; Lightfott, E.N.- ***Transport Phenomena***, Wiley, New York (1964).
[4] Curvers, J.; Rijks, R.; Cramers, C.; Knauss, K.; Larson, P.- **J. High Resolut. Chromatogr., Chromatogr. Commun., 8**, 607 (1985).
[5] Akporhonor, E.F.; Le Vent, S.; Taylor, D.R.- **J. Chromatogr., 405**, 67 (1987).
[6] Dal Nogare, S.; Langlois, W.E.- **Anal. Chem., 32**, 767 (1960).
[7] Gonzalez, F.R.; Nardillo, A.M.- **J. Chromatogr. A, 757**, 109 (1997).
[8] Snijders, H.; Janssen, H.G.; Cramers, C.- **J. Chromatogr. A, 718**, 339 (1995).
[9] ***Handbook of Chemistry and Physics***.- CRC Press, Boston, 72th ed. (1992).
[10] Ford, L.R.- ***Differential equations***, McGraw-Hill, New York, 2nd ed. (1955).
[11] Habgood, W.; Harris, W.E.- ***Programmed Temperature Gas Chromatography***, Wiley, New York (1966).
[12] Dose, E.V.- **Anal. Chem., 59**, 2414 (1987).